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# The Ozonizer Discharge as a Gas-Phase Advanced Oxidation Process

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## Abstract

Ozonizers have been used for over a century in water treatment and for about two decades in advanced oxidation. Ozonizers are fundamentally based on non-thermal plasmas, which are useful for generating reactive species (free radicals) in gas streams. Because radical-attack reaction rate constants are very large for many chemical species, entrained pollutants are readily decomposed by these radicals. Non-thermal plasmas can generate both oxidative and reductive radicals; therefore, they show promise for treating a wide variety of pollutants. However, this application is only about a decade old, so more work is needed for optimizing and commercializing the process.

## Introduction

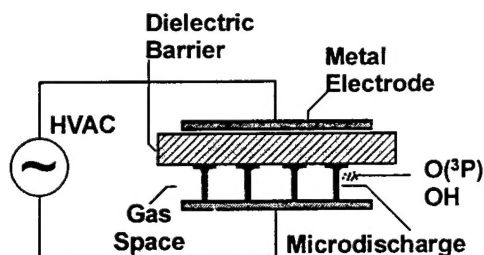
In the past several years, there has been increased interest in gas-phase pollution control arising from a larger body of environmental regulations and a greater respect for the environment. One promising class of pollution-control technologies is that called advanced oxidation processes (AOPs). Historically, AOPs first used highly reactive hydroxyl radicals (OH), generated from the photolysis of ozone ( $O_3$ ) or hydrogen peroxide ( $H_2O_2$ ), or the direct combination of  $O_3$  and  $H_2O_2$ , to treat recalcitrant water pollutants [1]. Therefore, ozone played a seminal role in the invention of AOPs. Recently, the definition of an AOP has been expanded to include processes which involve other free radicals, some of which are reductive rather than oxidative, and to the treatment of gaseous as well as aqueous-based effluents. AOPs show particular promise for the treatment of hazardous and toxic pollutants (e.g., volatile hydrocarbons and halocarbons and oxides of sulfur and nitrogen) because the reaction rates of free radicals with organic compounds can be orders of magnitude larger than a strong oxidizer like  $O_3$ . In the gas phase, free radicals and other highly reactive species can be generated with plasmas.

A plasma (in electrical terminology) is an ionized state of matter (sometimes called the *fourth state of matter*) containing electrons and ions. A plasma behaves much like an *electrical gas*, consisting of charged particles. Plasmas can be created thermally by heating ordinary matter to a temperature greater than about 10,000 C. In such a *thermal plasma*, all the species - electrons, ions, neutral atoms and molecules - are all in thermal equilibrium (i.e., at the same temperature). In contrast to a thermal plasma, a *non-thermal plasma* (or non-equilibrium plasma) is characterized by electrons which are not in thermal equilibrium with the other gas species. The electrons are *hot* (few to tens of eV temperature), while the ions and neutral gas species are *cold* (near-ambient temperature). The key idea in non-thermal plasma processing is to direct electrical energy into favorable gas chemistry through energetic electrons, rather than using the energy to heat the gas. Two common ways of creating a non-thermal plasma are by an electrical discharge in a gas or the injection of an energetic electron beam (e.g., 100 keV - 1 MeV) into a gas. Both processes create secondary plasma electrons, with a distribution of electron energies defined by an average electron energy (or electron temperature). An excellent non-thermal plasma source for generating atmospheric pressure, gas-phase, pollutant-decomposing species is the ozonizer discharge [2, 3].

This paper is intended to serve as an introduction to the subject of pollutant decomposition with the nonthermal plasmas generated by ozonizer discharges. Basic plasma and decomposition chemistry, laboratory experiments, and example applications are discussed.

## Ozonizer Discharges - Plasma Chemistry and Gaseous Electronics

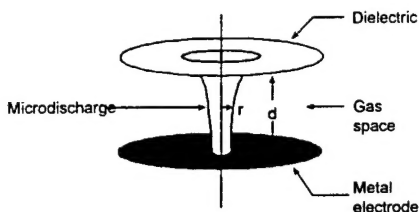
For over a century, ozonizers have been used for the large-scale generation of ozone for water treatment and bleaching applications. Ozonizers are frequently described in terms of corona discharges; however, they are more properly called dielectric-barrier discharges or silent electrical discharges [4]. A dielectric-barrier electrical discharge is produced when one or both electrodes bounding a thin gas space are covered with a dielectric (see Figure 1).



**Fig. 1:** Diagram of a single-dielectric-barrier discharge plasma reactor.

The barrier configuration was first reported in 1857 by von Siemens [5] and was named the silent discharge by Warburg [6] who investigated it around the turn of the century. The non-thermal plasma generated with silent electrical discharges has been applied to the destruction of hazardous or toxic chemicals for over a decade and, in this context, was named a silent discharge plasma (SDP) by Clothiaux et al [7] in 1984. An overview of the treatment of hazardous chemicals with SDP has been given recently by Rosocha [3].

The barrier arrangement provides a self-terminating discharge which is relatively independent of applied voltage waveshape. At gas pressures of order one atmosphere, gap spacings of order millimeters, and the application of alternating high voltage (e.g., 50 Hz to several kHz), a large number of "microdischarges", statistically spread in space and time over the electrode area, are created in the gas. Most evidence suggests that barrier discharges are generally described by a Townsend avalanche followed by a discharge streamer [4].

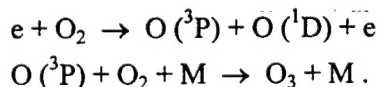


**Fig. 2:** Artist's depiction of a microdischarge streamer in a dielectric-barrier discharge.

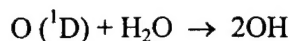
The microdischarge streamers (cylindrical current filaments with typical radius of order 100  $\mu\text{m}$ ) are transient discharges (e.g., lasting only a few nanoseconds for oxygen or air), fed by ionization and detachment and then arrested when charge build-up on the dielectric reduces the electric field in the streamer to the point where electron attachment becomes dominant. For microdischarges in pure oxygen and air, the breakdown reduced electric field strength is about 100-200 Td, while the average electron energy, electron

density, and current density are  $T_e \sim 3\text{-}5 \text{ eV}$ ,  $[e] \sim 10^{14}/\text{cm}^3$ , and  $J \sim 1 \text{ kA}/\text{cm}^2$ . Corona discharges produce plasmas similar to barrier discharges but take advantage of their natural electric-field inhomogeneity to terminate the discharge, rather than charge buildup on a dielectric barrier. Within a corona streamer, the  $E/N$  value is a strong function of position.

Free radicals, particularly oxygen-atom radicals, are effectively generated by such non-thermal plasmas and play a key role in the ozone-generation process:



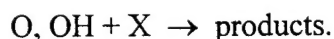
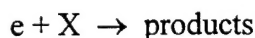
Other free radicals like the hydroxyl radical OH and nitrogen-atom radicals are also generated with ozonizer discharges in gases:



The yield of a particular radical species (i.e., the number of radicals produced per unit deposited plasma energy) will depend on factors such as the gas composition, the gas pressure, and the average electron temperature. In humid, atmospheric pressure air, the yields of  $\text{O} (^3\text{P})$ , OH, and N radicals in a typical silent discharge are of order 10, 1, and 1 per 100 eV of deposited energy, respectively [2, 3]. Usually pollutants in the concentration range of interest (100 to a few 1000s ppm) does not affect the electron distribution function or the associated electron temperatures or radical yields.

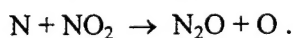
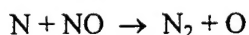
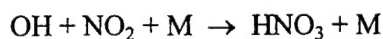
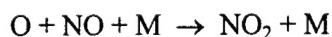
### *Basic Decomposition Chemistry*

The plasma-generated active species (radicals and secondary electrons) are the initiators of pollutant decomposition reactions. The two main decomposition channels for a gas-phase chemical pollutant X are direct electron impact or chemical (radical-promoted) attack:



The first path is expected to dominate at large contaminant concentrations (when a higher energy fraction is absorbed by the pollutant), while the second should dominate at smaller concentrations.

The decomposition chemistry for NO is tractable and can be largely described as follows [8]:



Oxidative-mode reactions involving O-atoms can trap total  $\text{NO}_x$  as NO and  $\text{NO}_2$ . Oxidative-mode reactions involving OH-radicals produce nitric acid  $\text{HNO}_3$ , which can be easily removed by a caustic scrubber. Reductive-mode reactions involving N-atoms instead drive more  $\text{NO}_x$  to  $\text{N}_2$  and  $\text{O}_2$  but require higher energy electrons than those normally produced by SDP reactors.  $\text{SO}_x$  removal [9] is similar and is favorably driven by O-atom and OH-radical oxidative reactions, producing easily-neutralized sulfuric acid as a terminal product. Ammonia addition is sometimes used to produce other useful products such as ammonium nitrate or ammonium sulfate (agricultural fertilizers).

Other molecules, like many VOCs, will often undergo a series of more complicated reactions before the final products result. The decomposition of a chlorocarbon like trichloroethylene is dominated by free-radical reactions at the relatively high E/N of a silent discharge [10]:



Strongly attaching molecules, like  $\text{CCl}_4$ , are preferentially decomposed by dissociative electron attachment at low E/N [11]

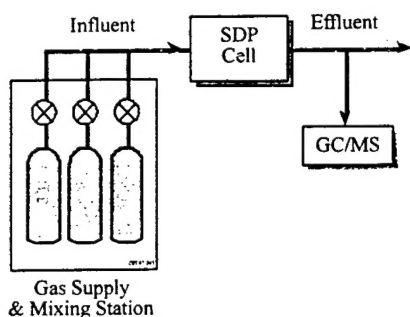


Decomposition is not necessarily complete treatment - the goal is to produce less toxic or more easily managed final products. Byproducts must also be considered (e.g.,  $\text{COCl}_2$  is toxic but is easily removed by reactions with water). A key advantage of the SDP process is the ability to simultaneously remove multiple pollutants. However, the plasma-initiated removal chemistry of a particular compound or mixture of compounds can be quite complicated and will not be addressed here in detail. For more information, the reader is referred to the literature.

## Methods of Investigation

### Laboratory Investigation Methods

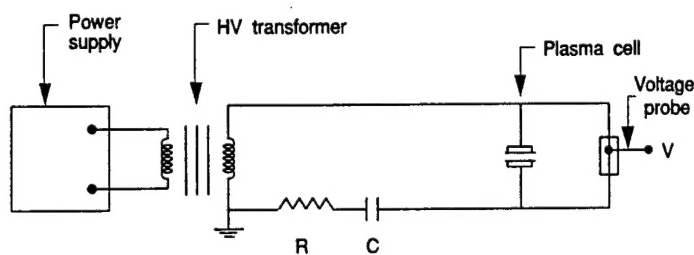
A typical laboratory setup for studying the decomposition of gas-phase pollutants with silent discharges is shown in Figure 3. An influent surrogate gas mixture representing the contaminant of interest is passed through the plasma cell and the degree of decomposition and treatment byproducts are measured with an instrument like a gas chromatograph - mass spectrometer.



**Fig. 3:** Schematic diagram of laboratory setup for SDP pollutant-decomposition experiments.

In our laboratory, we normally employ an electrical circuit similar to that depicted in Figure 4 for driving the SDP cell. As pointed out in the next section, it is important to measure the plasma energy density because it is a key parameter for pollutant destruction. The energy density is the same as the plasma electrical power divided by the gas flow rate. The electrical power is measured with a high-voltage probe combined with a charge-measuring circuit. Integration of a charge-voltage (Q-V) plot obtained from these measurements gives the power [12]. A standard commercial flow-meter is used to measure the gas flow. In typical laboratory tests, the contaminant concentrations are a few ppm to a few 1000 ppm (by volume) and gas flows are  $\sim 10$  std lit/min.

Representative energy densities range from a few 10s J/std lit (for  $\text{NO}_x$  and some hydrocarbons) to a few kJ/std lit for some difficult-to-destroy chlorinated hydrocarbons. With this circuit, the power is varied by changing the operating frequency.



**Fig. 4:** Circuit schematic for typical laboratory dielectric-barrier discharge reactor.

### Field Investigation Methods

SDP reactors can be used to treat stack-gas or flue-gas emissions from various sources or industrial process gas streams. Because many compounds require considerable electrical energy for decomposition, practical applications must focus on appropriate matches for the technology. An application that we have investigated in field trails is the treatment of solvents or other volatile compounds extracted

from soil or groundwater. Figure 5 depicts a mobile SDP processor [13] that we employed to treat soil vapor extraction (SVE) off-gases that were pumped from contaminated soil through vacuum-coupled wells. The highest concentration contaminants at the test site (McClellan Air Force Base) were trichloroethylene (TCE), 1,1,1-trichloroethane (1,1,1-TCA), and perchloroethylene (PCE).



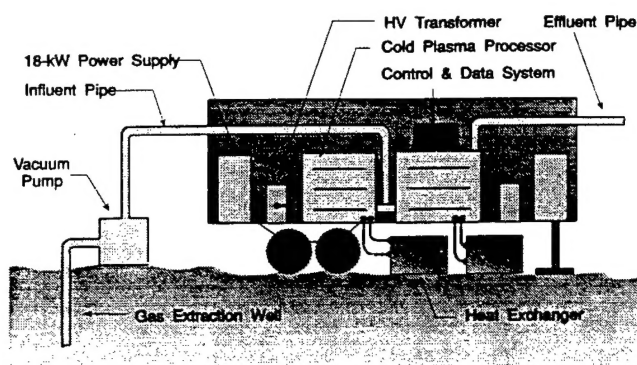


Fig. 5: Illustration of mobile SDP equipment for a VOC-treatment demonstration at McClellan AFB.

## Results and Discussion

In many electrical discharge plasma devices (like gas lasers, ozonizers, etc.), a key process parameter is the specific energy (plasma energy density) deposited in the gas. This is also true for the decomposition of a pollutant in an SDP reactor. Experiments with silent-discharge reactors have shown that the degree of removal of a particular contaminant depends on the applied plasma energy density and a characteristic energy-density parameter which is related to the target compound, the carrier gas, and the reduced electric field  $E/N$  for the

reactor [2, 3]. In many cases pollutant decomposition can be ideally expressed as

$$[X] = [X]_0 \exp(-\bar{E} / \beta),$$

where  $[X]_0$  is the initial pollutant concentration,  $[X]$  is the resulting concentration,  $\bar{E}$  is the applied specific energy (or plasma power divided by gas flow rate,  $P/Q$ ), and  $\beta$  is the e-fold energy density. Supplying one  $\beta$  to the reactor reduces the concentration by  $1/e$ ,  $2\beta$  by  $1/e^2$ , and so on. This particular equation strictly applies only when the rate of pollutant-decomposing radical scavenging is large compared to the rate of radical-pollutant attack [14]. In some other cases, the removal function additionally depends on the initial pollutant concentration. In an ideal case, when  $-\ln([X]/[X]_0)$  is plotted versus  $\bar{E}$ , a straight line of slope  $1/\beta$  results. For real cases, the plot is not necessarily a straight line, so such a slope-determined  $\beta$ -value is only an approximation. Figure 6 presents example decomposition data for two representative compounds, the flue gas nitric oxide (NO) and the chlorinated hydrocarbon TCE ( $C_2HCl_3$ ).

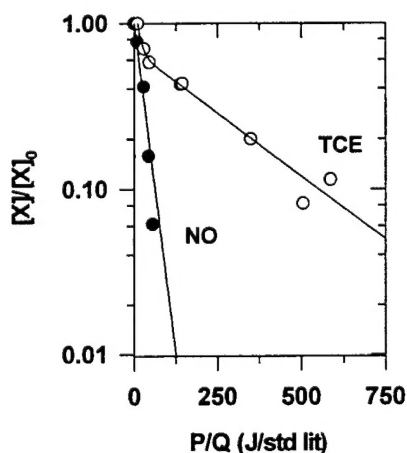


Fig. 6: Decomposition plots for 400 ppm NO in simulated engine-exhaust gas, after Wolf et al [15] and 190 ppm TCE in humid air, after Falkenstein [16].

In field tests with the mobile processor at 100% relative humidity, the TCE and PCE concentrations were reduced by greater than 1.5 and 1.0 decades, respectively. TCA, the hardest compound to destroy, was reduced by less than one decade. Drying the air stream and adding hydrogen both increased the performance.

## Conclusions

Many hazardous organic chemicals and the flue gases  $NO_x$  and  $SO_x$  are readily attacked by the free radicals generated in silent discharge plasmas (ozonizer discharges). In general, the degree of removal of a particular species is an exponential function of the plasma energy density. The characteristic e-fold energy density depends on both the pollutant and the carrier gas composition. The plasma-initiated decomposition chemistry of a particular compound or mixture can be complicated and has been the subject of both laboratory and field investigations. SDP treatment is expected to be particularly advantageous for the simultaneous removal of multiple pollutants. Ozonizers

have been used for more than a century but this application is only about a decade old. Therefore, more work is needed for process optimization and technology commercialization.

## References

1. W.H. Glaze, J.W. Kang, and D.H. Chapin, "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation," *Ozone: Science & Engineering*, **9**, pp. 335-352 (1987).
2. L.A. Rosocha, "Processing of Hazardous Chemicals Using Silent Electrical Discharge Plasmas," Chapter 11 in *Environmental Aspects in Plasma Science*, edited by W. Manheimer, L.E. Sugiyama, and T.H. Stix, American Institute of Physics Press, Woodbury, NY (1997).
3. L.A. Rosocha, G.K. Anderson, L.A. Bechtold, J.J. Coogan, H.G. Heck, M. Kang, W.H. McCulla, R.A. Tennant, and P.J. Wantuck "Treatment of Hazardous Organic Wastes Using Silent Discharge Plasmas," *Proceedings of NATO Advanced Research Workshop on Non-Thermal Plasma Techniques for Pollution Control, Series Springer-Verlag, Berlin & Heidelberg, NATO ASI SeriesG: Ecological Sciences, Vol. 34, Part B: Electron Beam and Electrical Discharge Processing*, edited by B.M. Penetrante and S.E. Schultheis, pp. 281-308 (1993).
4. B. Eliasson and U. Kogelschatz, "Modeling and Applications of Silent Discharge Plasmas," *IEEE Trans. Plasma Sci.*, **19**, pp. 309-322 (1991).
5. W. von Siemens, "Über die Elektrostatische Induktion und die Verzögerung des Stromes in Flaschendrahten", *Poggendorff's Ann. der Physik und Chemie* **102**, 66 (1857).
6. E. Warburg "Über die ozonisierung des sauerstoffs durch stille elektrische entladungen," *Ann. d. Phys.* **13**, pp. 464-476 (1904).
7. E.J. Clothiaux, J.A. Koropchack, and R.R. Moore, "Decomposition of an organophosphorus material in a silent electrical discharge," *Plasma Chemistry and Plasma Processing*, **4**, pp. 15-20 (1984).
8. See articles in B.M. Penetrante and S.E. Schultheis, editors, *Non-Thermal Plasma Techniques for Pollution Control, NATO ASI Series, Vol. G34, Parts A & B*, Springer-Verlag, Berlin & Heidelberg (1993).
9. I. Sardja and S.K. Dhali, "Plasma oxidation of SO<sub>2</sub>," *Appl. Phys. Lett.* **56**, pp. 21-23 (1990).
10. D. Evans, L.A. Rosocha, G.K. Anderson, J.J. Coogan and M.J. Kushner, "Plasma remediation of trichloroethylene in silent discharge plasmas", *J. Appl. Phys.* **74** (9), pp. 5378-5386 (1993).
11. D.G., Storch, M.B. Chang, M.J. Rood, and M.J. Kushner, "Modeling and diagnostics of dielectric barrier discharge destruction of CCl<sub>4</sub>," *Unpublished progress report to Los Alamos National Laboratory* (1991).
12. T.C. Manley, "The electric characteristics of the ozonator discharge," *Trans. Electrochemical Soc.* **84**, p. 83 (1943).
13. L.A. Rosocha, J.J. Coogan, R.A. Korzekwa, D.A. Secker, R.F. Riemers, P.G. Herrmann, P.J. Chase, M.P. Gross, and M.R. Jones, "Field Demonstration and Commercialization of Silent Discharge Plasma Air Pollutant Control Technology", *Proceedings of 2nd International EPRI/NSF Symposium on Environmental Applications of Advanced Oxidation Technologies*, Electric Power Research Institute (to be published).
14. J.R. Bolton, K.G. Bircher, W. Tumas, and C.A. Tolman, "Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Processes," *Journal of Advanced Oxidation Technologies*, **1**, pp. 13-17 (1996).
15. O. Wolf et al, "Experimentelle Untersuchungen an dielektrisch behinderten Entladungen zur Schadstoffentfernung aus Abgasen (Experimental Investigations of the Removal of Toxic Exhaust Gas Components by Dielectric Barrier Discharges)," Poster P 85, BFPT-7 (1996).
16. Z. Falkenstein, "Fundamental Studies on the Combined (V)UV-Non-Thermal-Plasma Treatment of Air Pollutants," Thesis, University of Karlsruhe & Los Alamos National Laboratory, LA-UR-96-2219 (July 1996).

## Key Words

Ozonizer discharges, Silent discharges, Advanced oxidation processes, Air pollutants, Free radicals.